



(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 1 094 034 A1

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:  
**25.04.2001 Bulletin 2001/17**

(51) Int. Cl.<sup>7</sup>: **C01G 45/00**

(21) Application number: **00915359.4**

(86) International application number:  
**PCT/JP00/02211**

(22) Date of filing: **06.04.2000**

(87) International publication number:  
**WO 00/61495 (19.10.2000 Gazette 2000/42)**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE**

- Kamada, Tsuneyoshi  
Takehara-shi, Hiroshima 725-0022 (JP)
- Nakashima, Takuya,  
Matsushita Elec. Ind. Co. Ltd.  
Kadoma-shi, Osaka 571-8501 (JP)
- ARIMOTO, Shinji,  
Matsushita Elec. Ind. Co. Ltd.  
Kadoma-shi, Osaka 571-8501 (JP)

(30) Priority: **08.04.1999 JP 10127299**  
**08.04.1999 JP 10127399**

(74) Representative:  
**Strehl Schübel-Hopf & Partner**  
**Maximilianstrasse 54**  
**80538 München (DE)**

(71) Applicants:

- Mitsui Mining & Smelting Co., Ltd.  
Tokyo 141-8584 (JP)
- Matsushita Electronics Corporation  
Kadoma-shi, Osaka 571-8501 (JP)

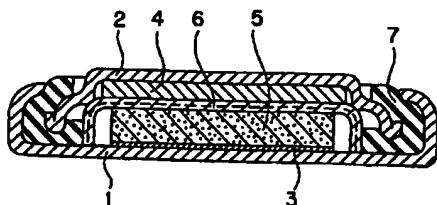
(72) Inventors:

- Numata, Koichi  
Takehara-shi, Hiroshima 725-0024 (JP)

**(54) METHOD FOR PREPARING LITHIUM MANGANATE HAVING SPINEL STRUCTURE**

(57) The process for preparing spinel-type lithium manganate according to the present invention is constituted by a process to admix the electrolyzed manganese dioxide, which is obtained by neutralizing manganese dioxide precipitated by means of electrolysis with any of potassium hydroxide, potassium carbonate and lithium hydroxide, and a lithium material and a process to subject the resulting mixture to a sintering process.

F i g . 1



EP 1 094 034 A1

**Description****Field of Invention**

5 [0001] The present invention is directed to a process for preparing spinel-type lithium manganate, and more specifically to a process for preparing spinel-type lithium manganese, from which eluting amount of manganese after prepared it into an anode material for non-aqueous electrolyte secondary battery is reduced, and which can improve performance of the battery under high temperature, such as preservation property and cycle property under high temperature.

10 **Background Art**

[0002] Based on recent rapid shift to miniaturized and cordless electronic hardware, such as personal computers and telephones, a need for using secondary batteries as a driving power source is becoming very intensive. Among the 15 secondary batteries, the biggest interest is directed to non-aqueous electrolyte containing secondary battery since it can be the smallest in size and can generate high energy density. As the anode material for non-aqueous electrolyte containing secondary battery which facilitates such desires as described above, lithium cobaltate ( $\text{LiCoO}_2$ ), lithium nickelate ( $\text{LiNiO}_2$ ), lithium manganate ( $\text{LiMn}_2\text{O}_4$ ), etc. can be used, for example. Each of these complex oxides has a voltage more than 4 V to lithium, and therefore, a battery having high energy density can be obtained by using any of such 20 complex oxides.

[0003] Among the complex oxides described above,  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  have a theoretical capacity of more or less 280 mAh/g, while  $\text{LiMn}_2\text{O}_4$  has a smaller theoretical capacity of 148 mAh/g. However,  $\text{LiMn}_2\text{O}_4$  can be suitably used for EV use because the resource of the raw material, manganese dioxides, is plenty and is cheaper in cost as well as no cause of thermal instability at charging like  $\text{LiNiO}_2$ .

25 [0004] However, lithium manganate ( $\text{LiMn}_2\text{O}_4$ ) has a problem of elution of Mn therefrom at a high temperature, which gives inferior battery property, such as preservation and cycle property under high temperature.

[0005] Therefore, it is an object of the present invention to provide a process for preparing spinel-type lithium manganate, which can reduce the eluting amount of manganese at charging when it is used as an anode material for non-aqueous electrolyte containing secondary battery and can improve the battery property under high temperature, such 30 as preservation and cycle properties under high temperature, an anode material composed of the lithium manganate and a non-aqueous electrolyte containing secondary battery using the said anode material.

**Disclosure of the Invention**

35 [0006] In solving the problem described above, the first invention of the present invention directing to a process for preparing spinel-type lithium manganate is characterized by admixing the electrolyzed manganese dioxide, which is prepared by neutralizing the manganese dioxide precipitated by means of electrolysis with any of potassium hydroxide, potassium carbonate and lithium hydroxide, and a lithium material and then subjecting the resulting mixture to a sintering process.

40 [0007] The second invention of the present invention is directed to the process specified in the first invention, wherein pH of the electrolyzed manganese dioxide being neutralized with either potassium hydroxide or potassium carbonate is 2 or more.

[0008] The third invention of the present invention is directed to the process specified in the first invention, wherein the electrolyzed manganese dioxide being neutralized with lithium hydroxide contains lithium in an amount of 0.02-0.5% 45 by weight.

[0009] The fourth invention of the present invention is directed to the process specified in the first, second and third inventions described above characterized in that the manganese dioxide is pulverized either before or after the neutralization with any of potassium hydroxide, potassium carbonate and lithium hydroxide.

[0010] The fifth invention of the present invention is directed to the fourth invention, wherein the average particle size 50 of the pulverized manganese dioxide is in a range of from 5 to 30 $\mu\text{m}$ .

[0011] The sixth invention of the present invention is directed to the process specified in any of the first to the fifth inventions, wherein the sintering process is operated at a temperature higher than 750°C.

[0012] The seventh invention of the present invention is directed to an anode material to be used for non-aqueous electrolyte containing secondary battery, wherein the anode material is composed of the spinel-type lithium manganate 55 obtained according to the process specified in any of the first to the sixth inventions.

[0013] The eighth invention of the present invention is directed to a non-aqueous electrolyte containing secondary battery, wherein the secondary battery is composed of an anode using the anode material for non-aqueous electrolyte containing secondary battery specified in the seventh invention, a cathode capable of occluding and de-occluding either

lithium alloy or lithium and non-aqueous electrolyte.

Brief explanation on Drawings

5 [0014]

Fig. 1 is longitudinal section of the coin-type non-aqueous electrolyte containing secondary battery specified in the Examples and Comparative examples described below.

10 Best Mode for carrying out the Invention

[0015] Now, the present invention is explained in detail with referring the attached drawings.

[0016] The present invention is explained hereinbelow, however, it should be noted that the scope of the present invention shall not be limited to the following description.

15 [0017] The process for preparing spinel-type lithium manganate according to the present invention is constituted by a process to admix the electrolyzed manganese dioxide being neutralized beforehand by treating manganese dioxide precipitated by means of electrolysis with any of potassium salt, lithium salt, etc. and a lithium material, and the following process to sinter the resulting mixture.

20 [0018] In the present invention, electrolyzed manganese dioxide is used as the manganese material for the spinel-type lithium manganate.

[0019] In the present invention, the electrolyzed manganese dioxide is obtained according to the following process. For example, for the electrolysis, manganese sulfate solution prepared at a fixed concentration is used as an electrolyte, a carbon plate is used for a cathode, and a titanium plate is used for an anode, then electrolysis is proceeded at a fixed current density while heating to electrically precipitate manganese dioxide around the cathode. Then the precipitated manganese dioxide is exfoliated from the anode and is then crushed to particles with a desired particle size, preferably to an average particle size of from 5 to 30 $\mu\text{m}$ .

25 [0020] In the non-aqueous electrolyte containing secondary battery, since the anode material is formed as a film having a thickness of more or less 100 $\mu\text{m}$ , cracking of the film may be caused if the particle size of the electrolyzed manganese dioxide is too large, and formation of an uniform film tends to be difficult. When providing the electrolyzed manganese dioxide having an average particle size of from 5 to 30 $\mu\text{m}$  as the material to produce the spinel-type lithium manganate, an anode material suitable to be used for film formation can be obtained without subjecting the manganese dioxide to an additional pulverization process. Therefore, it is estimated that the uniform distribution of potassium can be facilitated by neutralization of the micronized electrolyzed-manganese dioxide with a potassium salt.

30 [0021] The electrolyzed manganese dioxide pulverized into a desire particle size is then neutralized with either a potassium salt or a lithium salt, washed and followed by drying.

[0022] As the potassium salt used for the neutralization, any potassium salts can be used, but it is particularly preferable to use either potassium hydroxide or potassium carbonate. Additionally, there is no limitation in order for the pulverization and the neutralization, so the pulverization process may be carried out following to the neutralization process.

35 [0023] The pH of the electrolyzed manganese dioxide being neutralized with the potassium salt is 2 or more, and is more preferably in a range of from 2 to 5.5, and further preferable in a range of from 2 to 4. If the pH is too high, though eluting amount of manganese under high temperature can be reduced, the initial discharge capacity decreases, whereas, when the pH is lower than 2, the eluting amount of manganese cannot be lowered.

[0024] For the neutralization with a lithium salt, any lithium salts can be preferably used, however, it is particularly preferable to neutralize with lithium hydroxide.

40 [0025] There is no limitation in the order for the pulverization and the neutralization, thus pulverization may be done after completing the neutralization.

[0026] The amount of lithium contained in the electrolyzed manganese dioxide being neutralized with the lithium salt is preferably in a range of from 0.02 to 0.5% by weight. Though eluting amount of manganese at a high temperature may decrease, but the initial discharge capacity may be reduced when the lithium amount is more than 0.5% by weight, while the performance of the electrolyzed manganese dioxide may be insufficient when the lithium amount is less than 0.02% by weight.

45 [0027] In the process described above, the same sintering process as described in the process where employing the neutralization with a potassium salt as described above.

50 [0028] In the present invention, the spinel-type lithium manganate is obtained by admixing the electrolyzed manganese dioxide, which has been neutralized with either a potassium salt or a lithium salt beforehand, and the lithium material and subsequently sintering the resulting mixture. As the lithium material, lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), lithium sulfate ( $\text{LiNO}_3$ ), lithium hydroxide ( $\text{LiOH}$ ) and the like can be used, for example. The Li/Mn molar ratio for the electrolyzed manganese dioxide and the lithium material is preferably in a range of from 0.50 to 0.60.

[0029] For acquiring larger reaction area, it is also preferable to pulverize the electrolyzed manganese dioxide and the lithium material either before or after admixing them. The weighed and admixed materials can be used either directly or after making them into granules. The granulation may be done by either wet or dry method, and a process, such as extruding granulation, rotary granulation, fluid granulation, mixing granulation, spray drying granulation, pressure molding granulation, and flake granulation using rollers or the like, can be employed.

[0030] The materials obtained as described above are put into a furnace for sintering and are sintered at a temperature of from 600 to 1,000°C to obtain the spinel-type lithium manganate. For obtaining spinel-type lithium manganate in monolayer, it is sufficient to apply temperature around 600°C, however, it is preferable for the sintering to apply temperature higher than 750°C, and more preferably higher than 850°C, since the granule growth does not proceed when the temperature for sintering is lower than such range. As the furnace for sintering used in the process, rotary kiln, stationary furnace and the like can be given as the example. Time for the sintering should be more than 1 hour, and preferably 5 to 20 hours, in order to make the reaction uniform.

[0031] As described above, the spinel-type lithium manganate containing a certain amount of either potassium or lithium can be obtained. The spinel-type lithium manganate containing potassium is used as an anode material for the non-aqueous electrolyte containing secondary battery.

[0032] For the non-aqueous electrolyte containing secondary battery according to the present invention, a mixed material of the said anode material, a conductive material, such as carbon black, and a binding agent, such as teflon (Trade name for polytetrafluoro ethylene), is provided as an anode, either a lithium alloy or a material like carbon capable of occluding and de-occluding lithium is used as a cathode, and a mixture of lithium hexafluorophosphate ( $\text{LiPF}_6$ ) and a mixed solvent of ethylene carbonate and dimethylcarbonate or the like, or the one prepared into an electrolyte in gel, is used as the non-aqueous electrolyte, however, there is no limitation to such materials exemplified above.

[0033] Since the non-aqueous electrolyte containing secondary battery according to the present invention can control the elution of manganese at charging condition, it can improve battery performance under high temperature, such as preservation property under high temperature and cycle property under high temperature.

## 25 Examples)

[0034] Now, the present invention is definitely explained with referring the examples described below, however, it should be noted that the scope of the present invention shall not be limited to the description in the following examples.

30 Examples for employing neutralization with potassium salt)

[Example 1]

[0035] As an electrolyte for manganese, aqueous solution of manganese sulfate containing sulfuric acid at a concentration of 50g/L and manganese at a concentration of 40g/L was prepared. Heating was applied to the electrolyte so as to raise the temperature thereof to 95°C, and electrolysis was carried out by using a carbon plate as a cathode and a titanium plate as an anode at current density of 60 A/m<sup>2</sup>. Then, manganese dioxide electrically precipitated onto the anode was exfoliated and was crashed into chips with a size of less than 7 mm, and the chips were further pulverized into particles with an average particle size of 20μm.

[0036] The manganese dioxide in an amount of 20kg was washed with 20 liters water, then the water was removed, and another 20 liters water was added to the manganese dioxide. Then, potassium hydroxide in an amount of 75g was dissolved in the manganese dioxide solution, then the solution was subjected to neutralization for 24 hours while stirring, and the solution was then washed with water, filtrated and dried at 50°C for 12 hours. The pH and potassium content of the obtained powder were measured according to the method of JIS K-1467-1984, and the results are shown in Table 1 below.

[0037] The manganese dioxide with the average particle size of 20 μm in an amount of 1 kg was added with lithium carbonate so as to adjust Li/Mn molar ratio in the mixture at 0.54, and the mixture was then mixed and subjected to sintering process in a box-type furnace at 800°C for 20 hours to obtain the spinel-type lithium manganate.

50 [0038] An anode complex material was prepared by admixing the spinel-type lithium manganate in an amount of 80 parts by weight obtained as described above, carbon black in an amount of 15 parts by weight as a conductive agent and polytetrafluoro ethylene in an amount of 5 parts by weight as a binding agent.

[0039] By using the anode complex material, a coin-type non-aqueous electrolyte containing secondary battery shown in Fig. 1 was prepared. As shown in Fig. 1, a current collector 3 made of stainless steel is attached by means of spot welding onto the interior wall of an anode case 1 made of stainless steel, which is resistant to an organic electrolyte. An anode 5 composed of the said anode complex material is sealed with pressure onto the upper side of the current collector 3. On the upper side of the anode 5, a separator 6 made of microporous polypropylene resin being sopped in the electrolyte is located. At the opening part of the anode case 1, a closing cap 2, of which lower side a cath-

ode 4 composed of metal lithium is attached, is located in between the anode case and a gasket 7 made of polypropylene. The closing cap 2 is also functioning as a cathode terminate and is made of stainless steel as well as the anode case 1. The diameter of the battery is 20 mm, and the height is 1.6 mm. As the electrolyte, a solution prepared by equivalently mixing ethylene carbonate and 1,3-dimethoxy ethane in volume was used as a solvent, and lithium hexafluorophosphate was used as a solute and was added into the solvent at a rate of 1 mol/liter to obtain the electrolyte.

5 [0040] The battery obtained as describe above was subjected to charging tests. The charging test was carried out under a temperature of 20°C at a voltage ranging from 4.3 to 3.0 V, and the current density was fixed at 0.5 mA/cm<sup>2</sup>. Further, the battery was charged at a voltage of 4.3 V and was stored for 3 days at 80°C, and the preservation property of the battery was checked based on capacity preserving rate, which is calculated from the discharging capacity of the  
10 battery. The results of the initial discharging capacity and the preservation capacity maintaining rate are shown in Table 1 below.

[Example 2]

15 [0041] According to the same process described in the Example 1 except changing the adding amount of potassium hydroxide to 110g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganate was carried out. The pH and the potassium content after the neutralization is shown in Table 1. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and  
20 the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 1 presented below.

[Example 3]

25 [0042] According to the same process described in the Example 1 except changing the adding amount of potassium hydroxide to 140g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganate was carried out. The pH and the potassium content after the neutralization is shown in Table 1. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and  
30 the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 1 presented below.

[Example 4]

35 [0043] According to the same process described in the Example 1 except changing the adding amount of potassium hydroxide to 200g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganate was carried out. The pH and the potassium content after the neutralization is shown in Table 1. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and  
40 the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 1 presented below.

[Example 5]

45 [0044] According to the same process described in the Example 1 except changing the adding amount of potassium hydroxide to 280g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganate was carried out. The pH and the potassium content after the neutralization is shown in Table 1. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and  
50 the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 1 presented below.

[Example 6]

55 [0045] According to the same process described in the Example 2 except changing the temperature applied for the sintering to 900°C, synthesis for the spinel-type lithium manganate was carried out. The pH and the potassium content after the neutralization is shown in Table 1. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the

Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 1 presented below.

[Example 7]

5 [0046] According to the same process described in the Example 2 except changing the temperature applied for the sintering to 700°C, synthesis for the spinel-type lithium manganate was carried out. The pH and the potassium content after the neutralization is shown in Table 1. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the  
 10 Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 1 presented below.

[Comparative Example 1]

15 [0047] According to the same process described in the Example 1 except omitting the neutralization process for the electrolyzed manganese dioxide, namely the adding amount of potassium hydroxide is 0g, synthesis for the spinel-type lithium manganate was carried out. The pH and the potassium content after the neutralization is shown in Table 1. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 1 presented below.  
 20

[Table 1]

	JIS pH	K (% by weight)	Initial Discharging Capacity (mAh/g)	Preservation Capacity Maintaining Rate under High Temperature (%)
Example 1	2.5	0.17	121	72
Example 2	3.5	0.35	118	78
Example 3	4.5	0.60	115	81
Example 4	5.0	0.70	113	84
Example 5	6.0	1.00	108	86
Example 6	3.5	0.35	115	87
Example 7	3.5	0.35	118	71
Comparative Example 1	1.7	0	124	64

40

[Example 8]

45 [0048] According to the same process described in the Example 1 except changing the average particle size of the electrolyzed manganese dioxide at the pulverization to 5 µm, synthesis of the spinel-type lithium manganate was carried out. A coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the performance of the secondary battery was checked based on two current densities, 0.5 mA/cm<sup>2</sup> and 1.0 mA/cm<sup>2</sup>. The discharging capacity at the current density of 0.5 mA/cm<sup>2</sup> is fixed to 100, and the discharging capacity rate at the current density of  
 50 1.0 mA/cm<sup>2</sup> is represented as current load rate. The obtained current load rates are shown in Table 2 presented below.

[Example 9]

55 [0049] The same examination as done in the Example 8 was carried out for the coin-type non-aqueous electrolyte containing secondary battery prepared in the Example 1. The current load rate obtained is shown in Table 2 below.

## [Example 10]

[0050] According to the same process described in the Example 1 except changing the average particle size of the electrolyzed manganese dioxide at the pulverization to 30 µm, synthesis of the spinel-type lithium manganate was carried out. A coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1, and the same examination as done in the Example 8 was carried out for the obtained secondary battery. The current load rate obtained is shown in Table 2 below.

## 10 [Example 11]

[0051] According to the same process described in the Example 1 except changing the average particle size of the electrolyzed manganese dioxide at the pulverization to 35 µm, synthesis of the spinel-type lithium manganate was carried out. A coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1, and the same examination as done in the Example 8 was carried out for the obtained secondary battery. The current load rate obtained is shown in Table 2 below.

20

[Table 2]

25

	Average Particle Size (µm)	Current Load Rate (%)
Example 8	5	93
Example 9	20	88
Example 10	30	85
Example 11	35	74

30

## Examples for employing Neutralization with Lithium Salt)

## [Example 12]

35 [0052] As an electrolyte for manganese, aqueous solution of manganese sulfate containing sulfuric acid at a concentration of 50g/L and manganese at a concentration of 40g/L was prepared. Heating was applied to the electrolyte so as to raise the temperature thereof to 95°C, and electrolysis was carried out by using a carbon plate as a cathode and a titanium plate as an anode at current density of 60 A/m<sup>2</sup>. Then, manganese dioxide electrically precipitated onto the anode was exfoliated and was crashed into chips with a size of less than 7 mm, and the chips were further pulverized into particles with an average particle size of 20µm.

40 [0053] The manganese dioxide in an amount of 20kg was washed with 20 liters water, then the water was removed, and another 20 liters water was added to the manganese dioxide. Then, lithium hydroxide in an amount of 35g was dissolved in the manganese dioxide solution, then the solution was subjected to neutralization for 24 hours while stirring, then the solution was washed with water, filtrated and dried at 50°C for 12 hours. The lithium content in the obtained powder was measured and the results are shown in Table 3 below.

45 [0054] The manganese dioxide with the average particle size of 20 µm in an amount of 1 kg was added with lithium carbonate so as to adjust Li/Mn molar ratio in the mixture at 0.54, and the mixture was then mixed and subjected to sintering process in a box-type furnace at 800°C for 20 hours to obtain the spinel-type lithium manganate.

50 [0055] An anode complex material was prepared by admixing the spinel-type lithium manganate in an amount of 80 parts by weight obtained as described above, carbon black in an amount of 15 parts by weight as a conductive agent and polytetrafluoro ethylene in an amount of 5 parts by weight as a binding agent.

55 [0056] By using the anode complex material, a coin-type non-aqueous electrolyte containing secondary battery shown in Fig. 1 was prepared. As shown in Fig. 1, a current collector 3 made of stainless steel is attached by means of spot welding onto the interior wall of an anode case 1 made of stainless steel, which is resistant to an organic electrolyte. An anode 5 composed of the said anode complex material is sealed with pressure onto the upper side of the current collector 3. On the upper side of the anode 5, a separator 6 made of microporous polypropylene resin being sopped in the electrolyte is located. At the opening part of the anode case 1, a closing cap 2, of which lower side a cathode 4 composed of metal lithium is attached, is located in between the anode case and a gasket 7 made of polyp-

pyrene. The closing cap 2 is also functioning as a cathode terminate and is made of stainless steel as well as the anode case 1. The diameter of the battery is 20 mm, and the height is 1.6 mm. As the electrolyte, a solution prepared by equivalently mixing ethylene carbonate and 1,3-dimethoxy ethane in volume was used as a solvent, and lithium hexafluorophosphate was used as a solute and was added into the solvent at a rate of 1 mol/liter to obtain the electrolyte.

5 [0057] The battery obtained as describe above was subjected to charging tests. The charging test was carried out under a temperature of 20°C at a voltage ranging from 4.3 to 3.0 V, and the current density was fixed at 0.5 mA/cm<sup>2</sup>. Further, the battery was charged at a voltage of 4.3 V and was stored for 3 days at 80°C, and the preservation property of the battery was checked based on capacity preserving rate, which is calculated from the discharging capacity of the battery. The results of the initial discharging capacity and the preservation capacity maintaining rate are shown in Table  
10 3 below.

[Example 13]

15 [0058] According to the same process described in the Example 1 except changing the adding amount of lithium hydroxide to 55g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganese was carried out. The lithium content in the spinel-type lithium manganate is shown in Table 3. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are  
20 shown in Table 3 presented below.

[Example 14]

25 [0059] According to the same process described in the Example 1 except changing the adding amount of lithium hydroxide to 85g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganese was carried out. The lithium content in the spinel-type lithium manganate is shown in Table 3. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are  
30 shown in Table 3 presented below.

[Example 15]

35 [0060] According to the same process described in the Example 1 except changing the adding amount of lithium hydroxide to 130g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganese was carried out. The lithium content in the spinel-type lithium manganate is shown in Table 3. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are  
40 shown in Table 3 presented below.

[Example 16]

45 [0061] According to the same process described in the Example 1 except changing the adding amount of lithium hydroxide to 180g at the neutralization of the electrolyzed manganese dioxide, synthesis for the spinel-type lithium manganese was carried out. The lithium content in the spinel-type lithium manganate is shown in Table 3. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are  
50 shown in Table 3 presented below.

[Example 17]

55 [0062] According to the same process described in the Example 2 except changing the temperature applied for the sintering to 900°C, the synthesis for the spinel-type lithium manganate was carried out. The lithium content in the spinel-type lithium manganate is shown in Table 3. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temper-

ature of the secondary battery was measured, and the results are shown in Table 3 presented below.

[Example 18]

5 [0063] According to the same process described in the Example 2 except changing the temperature applied for the sintering to 700°C, the synthesis for the spinel-type lithium manganate was carried out. The lithium content in the spinel-type lithium manganate is shown in Table 3. Also, a coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the initial discharging capacity and the preservation capacity maintaining rate under high temperature of the secondary battery was measured, and the results are shown in Table 3 presented below.

10

[Table 3]

	Li (% by weight)	Initial Discharging Capacity (mAh/g)	Preservation Capacity Maintaining Rate Under High Temp. (%)
Example 12	0.02	123	69
Example 13	0.09	121	75
Example 14	0.13	118	78
Example 15	0.17	115	81
Example 16	0.23	110	84
Example 17	0.09	116	85
Example 18	0.09	121	68

[Example 19]

30 [0064] According to the same process described in the Example 1 except changing the average particle size of the electrolyzed manganese dioxide at the pulverization to 5 µm, synthesis of the spinel-type lithium manganate was carried out. A coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1. Then, the performance of the secondary battery was checked based on two current densities, 0.5 mA/cm<sup>2</sup> and 1.0 mA/cm<sup>2</sup>. The discharging capacity at the current density of 0.5 mA/cm<sup>2</sup> is fixed to 100, and the discharging capacity rate at the current density of 1.0 mA/cm<sup>2</sup> is represented as current load rate. The current load rates obtained are shown in Table 4 presented below.

35 [Example 20]

[0065] The same examination as done in the Example 8 was carried out for the coin-type non-aqueous electrolyte containing secondary battery prepared in the Example 1. The current load rate obtained is shown in Table 2 below.

[Example 21]

45 [0066] According to the same process described in the Example 1 except changing the average particle size of the electrolyzed manganese dioxide at the pulverization to 30 µm, synthesis of the spinel-type lithium manganate was carried out. A coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1, and the same examination as done in the Example 8 was carried out for the obtained secondary battery. The current load rate obtained is shown in Table 4 below.

50 [Example 22]

55 [0067] According to the same process described in the Example 1 except changing the average particle size of the electrolyzed manganese dioxide at the pulverization to 35 µm, synthesis of the spinel-type lithium manganate was carried out. A coin-type non-aqueous electrolyte containing secondary battery was prepared by using the spinel-type lithium manganate as the anode material according to the process disclosed in the Example 1, and the same examination as done in the Example 8 was carried out for the obtained secondary battery. The current load rate obtained is shown in Table 4 below.

[Table 4]

	Average Particle Size ( $\mu\text{m}$ )	Current Load Rate (%)	
5	Example 19	5	94
10	Example 20	20	89
15	Example 21	30	86
20	Example 22	35	76

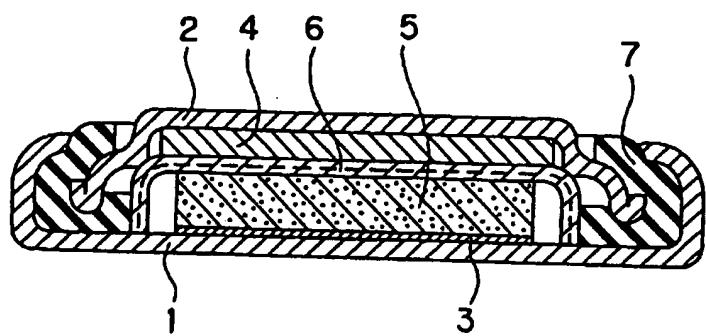
## Industrial Use

15 [0068] As described above, by using the spinel-type lithium manganate obtained according to the process specified in the present invention as the anode material for the non-aqueous electrolyte containing secondary battery, control of manganese elution from the battery at charging, improvement of high temperature battery property, such as preservation property under high temperature and cycle property under high temperature, and improvement of the current load rate of the secondary battery can be achieved.

## Claims

- 25 1. A process for preparing spinel-type lithium manganate characterized in that the spinel-type lithium manganate is prepared by admixing electrolyzed manganese dioxide, which is obtained by neutralizing manganese dioxide precipitated by means of electrolysis with any of potassium hydroxide, potassium carbonate and lithium hydroxide, and a lithium material and consequently by subjecting the mixture to a sintering process.
- 30 2. The process for preparing spinel-type lithium manganate according to claim 1, wherein pH of the electrolyzed manganese dioxide being neutralized with either potassium hydroxide or potassium carbonate is 2 or more.
- 35 3. The process for preparing spinel-type lithium manganate according to claim 1, wherein the electrolyzed manganese dioxide being neutralized with lithium hydroxide contains lithium in an amount of 0.02-0.5% by weight.
- 40 4. The process for preparing spinel-type lithium manganate according to any of claims 1 to 3, wherein the manganese dioxide is pulverized either before or after the neutralization with any of potassium hydroxide, potassium carbonate and lithium hydroxide.
5. The process for preparing spinel-type lithium manganate according to claim 4, wherein the average particle size of the pulverized manganese dioxide is in a range of from 5 to 30 $\mu\text{m}$ .
6. The process for preparing spinel-type lithium manganate according to any of claims 1 through 5, wherein the sintering process is operated at a temperature higher than 750°C.
- 45 7. An anode material for non-aqueous electrolyte containing secondary battery characterized by being composed of the spinel-type lithium manganate obtained according to the process described in any of claims 1 through 6.
- 50 8. A non-aqueous electrolyte containing secondary battery characterized by being constituted with an anode using the anode material for non-aqueous electrolyte containing secondary battery according to claim 7, a cathode capable of occluding or de-occluding lithium alloy or lithium and non-aqueous electrolyte.

F i o . 1



INTERNATIONAL SEARCH REPORT		International application No. PCT/JP00/02211
<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl <sup>7</sup> CO1G45/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl <sup>7</sup> CO1G45/00, H01M4/58, H01M4/02, H01M10/40		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsugyo Shinan Koho 1926-1996 Toroku Jitsugyo Shinan Koho 1994-2000 Kokai Jitsugyo Shinan Koho 1971-2000 Jitsugyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, 5698176, A (Duracell, Inc., Bethel, Conn), 16 December, 1997 (16.12.97) Claims; column 2, lines 46 to 62, implementation example & WO, 9640588, A & ZA, 9603652, A & AU, 9659825, A	1-8
PA	JP, 2000-048817, A (Matsushita Electric Ind. Co., Ltd.) 18 February, 2000 (18.02.00) Claims; implementation example	1-8
A	JP, 5-174823, A (Hitachi Maxell Ltd.), 13 July, 1993 (13.07.93), Claims; implementation example (Family: none)	1-8
A	JP, 10-116617, A (Toshiba Battery Co., Ltd.), 06 May, 1998 (06.05.98) Claims; implementation example (Family: none)	1-8
A	JP, 9-073902, A (Toshiba Battery Co., Ltd.), 18 March, 1997 (18.03.97) Claims; implementation example (Family: none)	1-8
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 26 June, 2000 (26.06.00)		Date of mailing of the international search report 11 July, 2000 (11.07.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.